

# **High Temperature Transfer Molding Resins: Status of PETI-298 and PETI-330**

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## **ABSTRACT**

Two phenylethynyl terminated oligomers designated PETI-298 and PETI-330 were developed at the NASA Langley Research Center and have emerged as leading candidates for composite applications requiring high temperature performance (i.e.  $\geq 288^{\circ}\text{C}$  for 1000 hours) combined with the ability to be readily processed into composites without the use of an autoclave or complex/lengthy cure or post-cure cycle. These high performance/high temperature composites are potentially useful on advanced aerospace vehicles in structural applications and as aircraft engine components such as inlet frames and compressor vanes. The number designation (i.e. 298, 330) refers to the glass transition temperature in degrees Celsius as determined on neat resin cured for 1 hour at  $371^{\circ}\text{C}$ . The resins are processable by non-autoclave techniques such as resin transfer molding (RTM), vacuum assisted RTM (VARTM) and resin infusion (RI). Both resins exhibit low complex melt viscosities (0.1-10 poise) at  $280^{\circ}\text{C}$  and are stable for  $\geq 2$  hours at this temperature. Typically, the resins are melted, de-gassed and infused or injected at  $280^{\circ}\text{C}$  and subsequently cured at  $371^{\circ}\text{C}$  for 1-2 hours. Virtually no volatiles are evolved during the cure process. The resin synthesis is straightforward and has been scaled-up to 25 kg batches. The chemistry of PETI-298 and PETI-330 and the RTM AS-4 and T-650 carbon fabric laminate properties, and those of BMI-5270 for comparison, are presented.

**KEY WORDS:** Resin Transfer Molding, High Temperature Polymers, Polyimides, PETI-330, PETI-298, High Temperature Laminates, RTM

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## 1. INTRODUCTION

High temperature organic polymers are needed for a variety of applications on advanced aerospace vehicles and propulsion systems. Aromatic polyimides are leading candidates for these types of applications due to their excellent combination of physical and mechanical properties [1,2]. These materials have traditionally been processed from solvent laden prepreg and required high pressure/autoclave processes concurrent with volatile removal to fabricate high quality, carbon fiber reinforced laminates. Consequently, the costs and processing difficulties associated with these materials have limited their use. The monomeric reaction approach, such as that used with PMR-15, has been practiced for many years as a means of obtaining processability and good quality composites. However, this approach suffers from the use of toxic monomers such as 4,4'-methylenedianiline and solvents that must be removed during composite fabrication and subsequently disposed of. PMR-15-type materials also suffer from complex and lengthy cure cycles as well as extended post-cures. In addition, due to the concentration and chemical structure of the reaction product formed during cure, brittleness and microcracking are often a problem in PMR-15-type composites. Bismaleimides (BMIs), such as 5250-4 and 5270-1, are processable by resin transfer molding (RTM), but their upper use temperature is in the range of 232°C falling between that of an epoxy and PMR-15. In addition, they require a lengthy post-cure, ~4-6 hours at 177°C or higher to achieve high glass transition temperatures ( $T_g$ s) [3,4].

An alternative approach that has received attention recently is the use of controlled molecular weight imide oligomers containing phenylethynyl groups (abbreviated as PETI for phenylethynyl terminated imide) [5-15]. The oligomers are free of toxic monomers and the problems associated with residual solvent and lengthy, complex cure and post-cure cycles are eliminated. The phenylethynyl group offers the advantages of being thermally unreactive to about 300°C, reacting rapidly at temperatures of 350-371°C without volatile evolution, and forming a product that provides good toughness, microcrack resistance and excellent thermo-oxidative stability. The disadvantage has been the availability and cost of suitable endcapping agents such as 4-phenylethynylphthalic anhydride (PEPA) for these materials. With the recent demonstration of the potential of these types of resins to offer an unprecedented combination of high temperature laminate performance with superior processing characteristics, the cost and availability of these materials is expected to improve dramatically.

PETI oligomers for high temperature RTM, vacuum assisted RTM (VARTM) and resin infusion (RI) have been under investigation since the late 1990s. To demonstrate the versatility and processing robustness of these resins, complex composite parts such as I-beams, F-frames and skin stringer panels have been fabricated using RTM and RI. VARTM has provided flat laminates with mechanical properties equivalent to laminates fabricated by RTM. Recent efforts have focused on increasing the use temperature by modifying the chemistry to effect as high a  $T_g$  as possible without causing an increase in melt viscosity [11,12,14]. An approach has been developed that focuses on using a combination of aromatic diamines to impart flexibility (for low melt viscosity) and rigidity (for high  $T_g$ ), a dianhydride and endcapping with PEPA [13].

Previous studies have indicated that an optimum calculated molecular weight is  $\sim 750$  g/mole (excluding the molecular weight of the endcapping agent) [7]. Since the diamines are in significant excess, they have the greatest impact on the melt viscosity and final  $T_g$  of the resin. To achieve this calculated molecular weight, a stoichiometric imbalance or molar ratio of  $\sim 0.50$  mole of dianhydride to 1.0 mole of diamines is required. This relatively high stoichiometric offset results in a multi-modal molecular weight distribution that contains a low molecular weight component that contributes significantly towards achieving low melt viscosity.

Over the past 15 years, polyimides from 2,3',3',4'-biphenyltetracarboxylic dianhydride (asymmetric isomer, a-BPDA) were shown to have lower melt viscosities and higher  $T_g$ s than the corresponding polymers from 3,3',4,4'-biphenyltetracarboxylic dianhydride (symmetric isomer, s-BPDA) [16-21]. This is presumably due to the highly irregular structure of the polyimide emanating from a-BPDA. In addition, a-BPDA based PETIs were shown to have lower melt viscosities and when cured, higher  $T_g$ s than the analogous PETIs based upon s-BPDA. However, due to the molecular weight range investigated, none of the a-BPDA derived PETIs had a melt viscosity low enough for RTM. Thus, a series of low molecular weight PETIs derived from a-BPDA were prepared in an attempt to obtain resins with RTM/VARTM processability and when cured, high  $T_g$ s and high laminate properties [11,12]. Since oligomers from this monomer offer the unusual combination of lower melt viscosity and higher  $T_g$  (as compared to the s-BPDA based imides), it was an obvious choice to include in the high temperature PETI RTM formulations. Based on our previous work [11,12], PETI-330 was selected as a composite matrix resin for further evaluation.

PETI-298 and PETI-330, and for comparison purposes, BMI-5270 laminates were fabricated by RTM using un-sized carbon fabric (AS-4 and T650-35). The sizing on the fabric was removed thermally prior to laminate fabrication. The chemistry of PETI-298 and PETI-330 and the RTM laminate processing conditions and properties of PETI-298, PETI-330 and BMI-5270 are presented herein.

## **2. EXPERIMENTAL**

### **2.1 Starting Materials**

The syntheses of PETI-298 and PETI-330 have been reported previously [7-10]. BMI-5270 was obtained from Cytec Engineered Materials. AS-4 and T-650-35 8 harness satin (8HS) carbon fiber fabric were obtained from Fabric Development, Inc.

### **2.2 Laminates**

Prior to laminate fabrication, the fabric sizing was removed by bagging the fabric in Kapton™, sealing with a high temperature sealant, and heating at 400°C for 2 hr under vacuum. BMI-5270 laminates were fabricated by RTM by de-gassing the resin at 140°C for  $\sim 0.5$  hr, injecting at  $\sim 160^\circ\text{C}$  into AS-4 and T650-35 8HS fabric and subsequently curing for 4 hrs at 191°C followed by a 4 hr post-cure at 250°C. Laminates of PETI-298 and PETI-330 were also made by RTM using AS-4 and T650-35 8HS fabric. The resins were injected into the unsized 8HS carbon fiber fabric positioned on an Invar tool using a high temperature injector. The

maximum processing parameters of the injector, designed and built by Radius Engineering according to Lockheed Martin specifications, are a temperature of 288°C, flow rate of 500 cc/min, and pressure of 2.75 MPa. The tool containing the fabric was loaded into a press, heated to 316°C, and held at 316°C for 1.5 hrs prior to resin injection. The PETI resins were de-gassed in the injector by heating to 288°C and holding for 1 hr prior to injection. The de-gassing step was required primarily to remove moisture, residual solvent, and air from the resin. The molten resin was used to infiltrate 8-ply stacks of unsized 8HS fabric [equivalent to 16 plies of unitape, lay-up of (0/90)<sub>4S</sub>] in an Invar tool under 1.34 MPa hydrostatic pressure during the entire process cycle. After the resin was injected at 288°C at a rate of 200 cc/min, the part was held under 1.34 MPa of hydrostatic pressure while heating to 371°C and holding at 371°C for 1 hr. The 33 cm x 36 cm laminates were cooled under pressure. The laminates were ultrasonically scanned (C-scanned, pulse echo), cut into specimens, and tested for mechanical properties. The laminates were examined for microcracks by a microscope up to 400X magnification. Resin content, fiber volume, and void content were determined by acid digestion using a 1:1 (w/w) solution of concentrated sulfuric acid and 30% hydrogen peroxide. Open hole compression (OHC) properties (Northrup Grumman Test) were determined on 25.4 cm by 3.81 cm specimens with a 0.64 cm hole in the center. Un-notched compression (UNC) properties (Boeing Test, BSS 7260) were determined on 8.08 cm by 1.27 cm specimens. Short beam shear (SBS) strength (ASTM D2344-84) was determined on 0.64 cm by 1.91 cm specimens. Unstressed specimens were aged at 288°C in a forced air oven. Five specimens were tested under each condition.

### **2.3 Other Characterization**

DSC was performed on powdered samples using a Shimadzu DSC-50 thermal analyzer at a heating rate of 20°C/min with the  $T_g$  taken at the mid-point of the inflection of the differential heat flow ( $\Delta H$ ) versus temperature curve. PETI-298 and PETI-330 were cured at 371°C for 1 hr in a sealed aluminum pan and quenched prior to obtaining the cured  $T_g$ s. Thermal mechanical analysis (TMA) was performed from 25°C to 400°C using a Seiko model TMA210 at a heating rate of 10°C/min. Neat resin specimens were obtained from cured resin flash inside the RTM tool. Dynamic mechanical thermal analysis (DMTA) was performed using a Seiko model DMS210 from -150°C to 400°C at a heating rate of 10°C/min. Cured thin film resin samples were obtained from underneath the knock-out plate in the RTM tool following laminate fabrication. The storage moduli ( $E'$ ) and loss moduli ( $E''$ ) were obtained as a function of temperature. TGA was performed on powder samples in air and nitrogen at a flow rate of 50 cm<sup>3</sup>/min. The samples were heated at 20°C/min to 100°C, held for 1 hr, and subsequently heated to 600°C at a heating rate of 2.5°C/min. Rheological measurements were conducted on a Rheometrics System 4 rheometer at a heating rate of 4°C/min. Specimen disks (2.54 cm in diameter and 1.5 mm thick) were prepared by compression molding imide powder at room temperature. The compacted resin disk was subsequently loaded in the rheometer fixture with 2.54 cm diameter parallel plates. The top plate was oscillated at a variable strain and a fixed angular frequency of 100 rad/sec while the lower plate was attached to a transducer, which

recorded the resultant torque. Complex melt viscosity ( $\eta^*$ ) as a function of time (t) was measured at several temperatures.

### 3. RESULTS AND DISCUSSION

#### 3.1 Synthesis of PETI-298 and PETI-330

The development of PETI-298 and PETI-330 emanated from an effort under the High Speed Civil Transport (HSCT) program to develop PETI resins that could be used to fabricate carbon fiber reinforced composites by low viscosity techniques such as RTM and RI. This work led to the development of the first PETIs that were processable by RTM and exhibited good mechanical properties [7]. However, due to the HSCT application requirements, a cured  $T_g$  of  $\sim 250^\circ\text{C}$  was acceptable. At the end of the HSCT program, this technology was transitioned to a space transportation program to develop resins processable by RTM, RI and VARTM with higher cured  $T_g$ s and good mechanical properties for future composite applications on reusable launch vehicles (RLVs). At this time, the chemistry was still based on s-BPDA, but other diamines were investigated to increase the cured  $T_g$  while maintaining RTM processability. One monomer used in the early RTM PETI resin chemistry was 1,3-bis(3-aminophenoxyphenyl)benzene. Although this monomer was known to provide improvement in processability [22,23], it also contributed to a low  $T_g$ . Consequently, the use of this monomer was terminated and work was initiated on incorporating the other isomers of APB (1,3,4-APB and 1,4,4-APB) into the oligomer and determining the effects upon RTM processability, cured resin  $T_g$ , and laminate properties [8,9]. Compositions containing the 1,4,4-APB monomer had higher cured  $T_g$ s as expected but the melt viscosities of the resins also increased by several orders of magnitude. Compositions prepared with 1,3,4-APB provided resins with low and stable melt viscosities amenable to RTM processability and high cured  $T_g$ s. Thus this diamine was selected for use with the next generation PETI RTM resins and is a key component in both PETI-298 and PETI-330.

Since a-BPDA derived PETIs were shown to exhibit low melt viscosity and when cured, high  $T_g$ s, a series of new PETIs based upon a-BPDA were prepared and evaluated for RTM processability. The chemistry of PETI-330 evolved from this work. It makes use of the unique features of a-BPDA in combination with 1,3,4-APB and 1,3-PDA. The imide oligomers are synthesized in a one-pot reaction and remain soluble in warm NMP (up to  $\sim 35$ -40% solids). The solids are isolated by precipitation into water and subsequently washed in water and dried  $\sim 135^\circ\text{C}$ . Precipitation of the imide oligomer into organic solvent such as acetone or methanol is not recommended since low molecular weight species are extracted from the resin. This has a negative impact on the melt flow behavior and can result in an increase in the melt viscosity by more than 1 order of magnitude [7]. The synthesis of both of these resins is straightforward and has been scaled-up to 25 kg batches.

#### 3.2 Characterization of PETI-298 and PETI-330

The number designation after PETI refers to the cured  $T_g$  of the neat resin in  $^\circ\text{C}$ . The  $T_g$  was obtained from neat resin powder cured for 1 hr at  $371^\circ\text{C}$  in an aluminum pan in a DSC cell.

The experiment was conducted at a heating rate of 20°C/min and the  $T_g$  was reported at the mid-point of the inflection of the  $\Delta H$  versus temperature curve. Under these conditions the baseline deflection associated with the  $T_g$  can span a temperature range of 15-25°C. Deviations in the reported cured resin  $T_g$ s are expected when different measurement techniques and different heating rates are used. The characterization of the cured resin  $T_g$  was determined by three different techniques and the results are presented in Table 1. In some cases, the uncured neat resin powders exhibited transient crystalline melting transitions on initial heat-up by DSC. These transitions occur at temperatures well below the cure temperature and cannot be recovered by annealing. For the TMA and DMTA experiments, the neat resin, cured for 1 hr at 371°C, was obtained directly from the RTM tool after laminate fabrication.

Table 1. Characterization of Neat Resin

Resin	$T_g$ , °C by DSC <sup>1</sup>	$T_g$ , °C by TMA <sup>2,3</sup>	$T_g$ , °C by DMTA <sup>2,4</sup>
PETI-298	298	281	312
PETI-330	330	313	326
BMI-5270	----	249 (287 <sup>5</sup> )	276

1. Obtained on neat resin powders after 1 hr at 371°C in an aluminum pan at a heating rate 20°C/min
2. Cured resin obtained from inside RTM tool, cured for 1 hr at 371°C
3. TMA heating rate 10°C/min
4. DMTA heating rate 10°C/min, frequency 0.1-10 hertz, (tan delta)
5. By TMA as reported in reference 3

As part of the quality control process, PETI-298 and PETI-330 were analyzed for volatile content, cured  $T_g$  and complex melt viscosity. The cured  $T_g$  was determined by DSC on neat resin powder samples under the conditions previously described. The volatile content was determined by measuring the weight loss on uncured neat resin powders by dynamic TGA under the conditions described in the experimental section. Typically, these resins exhibited a 1% weight loss between 300 and 350°C. Higher weight losses at these temperatures were an indication that the samples were not fully dry.

The complex melt viscosity ( $\eta^*$ ) was measured using PETI-298 and PETI-330 discs compression molded at room temperature. The test chamber of the rheometer was at room temperature for specimen insertion. The specimen was heated from 23 to 280°C at a heating rate of 4°C/min and held for 2 hrs at 280°C to assess melt stability and then heating was continued to 371°C at the same heating rate and held for 0.5 hr to cure the material.

The melt viscosity of PETI-298 was generally in the range of 1-10 poise at 280°C and did not change appreciably at this temperature indicating excellent melt stability. This is because the phenylethynyl group reacts very slowly at this temperature. The melt stability at the minimum viscosity was critical for processing of large parts by RTM, VARTM and RI. These PETI materials have an excellent processing window (i.e. temperature difference between where the

minimum melt viscosity occurs and onset of cure) and consequently exhibited excellent robustness in processing. Other endcapping groups that can be used with imide oligomers such as nadic or maleimide begin to cure at lower temperatures with a consequent melt viscosity increase. The PETI-330 exhibits similar melt viscosity behavior to the PETI-298 although the melt viscosity is typically less than the PETI-298 by nearly one order of magnitude [10,11].

### 3.3 Laminates

The laminates were made with 8 plies of unsized 8HS carbon fabric with a (0/90)<sub>4S</sub> lay-up (quasi-isotropic). Fabric sizing was removed by heating the fabric at 400°C for 2 hrs under vacuum prior to insertion in the tool. The PETI powder was charged to the resin chamber, heated to 280°C and de-gassed prior to injection into the tool. Laminate fabrication involved injecting the molten resin at ~280°C into the preheated tool followed by a cure at 371°C for 1 hr under ~1.4 MPa hydrostatic pressure. All of the laminates were of high quality as determined by C-scan and photomicroscopy. Acid digestion was used to determine the resin content of each panel. The panels were machined into specimens and tested according to ASTM or other well-documented procedures. Laminate characterization of AS-4 carbon fabric composites based on the analysis of two or more laminates is presented in Table 2.

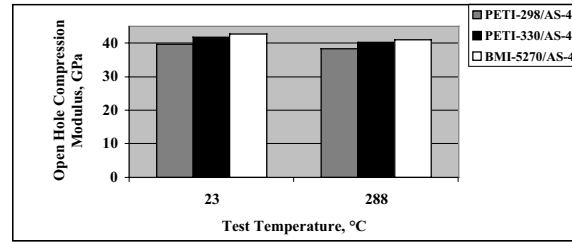
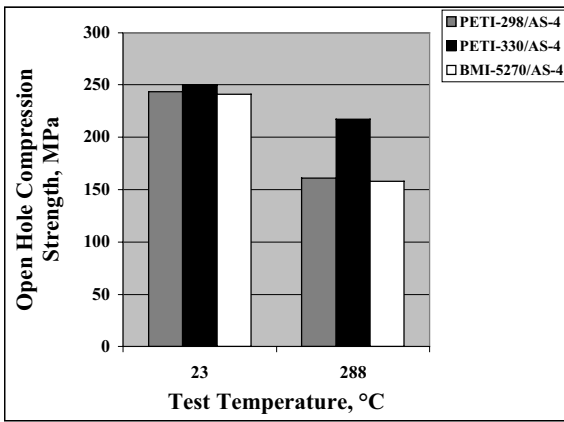
Table 2. AS-4 Laminate Characterization

Matrix	Fiber Volume, %	Voids, %	Microcracks/inch	T <sub>g</sub> , °C (TMA)
PETI-298	57.3-60.5	0.7-1.7	N/D	275-287
PETI-330	56.8-58.1	1.7-2.5	N/D	310-320
BMI-5270	58.1-60.4	0.5-0.8	5-162	238-248

N/D = Not detected.

Good consistency was obtained in laminate fabrication with respect to fiber volume and void content as determined by acid digestion. Examination for microcracks on as-processed PETI-298 and PETI-330 laminates indicated no microcracking. A broad range of T<sub>g</sub>s was determined by TMA on laminates and as-expected, they were lower than those determined on cured neat resin powders by DSC.

The mechanical properties of PETI-298, PETI-330 and BMI-5270 on AS-4 fabric are presented in Figures 1-6. The properties of the BMI-5270, a RTM processable matrix resin from Cytec Engineered Materials, are included for comparison purposes. The cured resin has a reported cured T<sub>g</sub> of ~287°C [3]. The open hole compression (OHC) strengths and moduli at room temperature and 288°C are presented in Figures 1 and 2, respectively. The room temperature OHC strengths of all three are comparable. However at 288°C, the PETI-330 exhibited significantly better retention of room temperature (RT) OHC strength (~90%) whereas the other two retained about ~65% of their room temperature strength. The OHC moduli of all three were comparable at room temperature and 288°C. This was not surprising since modulus



Figures 1 and 2. OHC strength and modulus of PETI-298, PETI-330 and BMI-5270/AS-4 8HS laminates.

is a fiber-dominated property. The short beam shear (SBS) strengths at 23, 232 and 288°C are presented in Figure 3. As was the case with the OHC strengths, the PETI-330 exhibited much higher retention of strength with temperature followed by the PETI-298 and the BMI-5270. The property retention was most likely a reflection of the difference in the  $T_g$ s. The resin with the highest  $T_g$  would be expected to exhibit the best retention of properties. The test temperature of

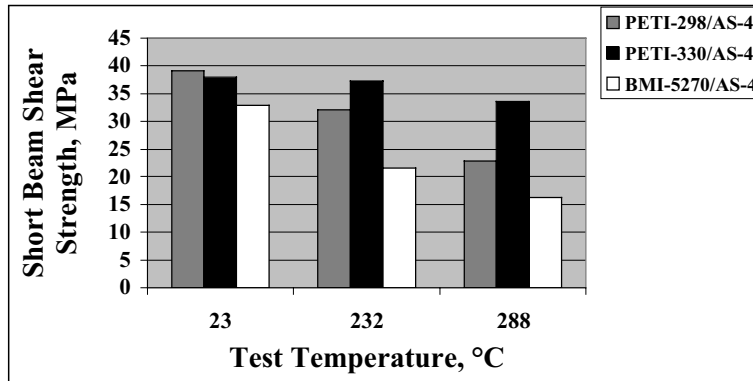
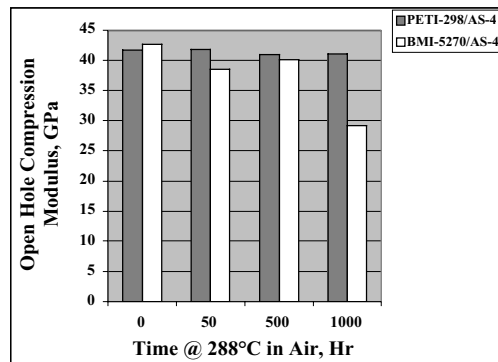
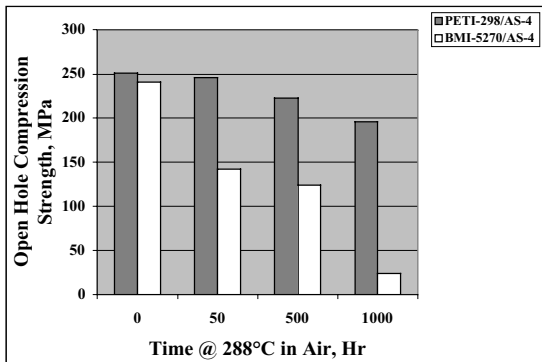


Figure 3. SBS strength of PETI-298, PETI-330 and BMI-5270/AS-4 8HS laminates.



Figures 4 and 5. RT OHC strength and modulus after isothermal aging at 288°C in air.



330/AS-4 288°C was within 10°C of the cured  $T_g$  of the PETI-298 and is the cured  $T_g$  of BMI-5270. Room temperature UNC strengths for the PETI-298 and PETI-330 laminates were 503 and 442 MPa, respectively.

It should be pointed out that the thermooxidative stability of the PETI resins is controlled by the product emanating from the endcapping (phenylethynyl) group. The nature and chemical structure of the cured product is unknown but is thought to be comprised of a polyene-type structure. It has been reported that the reaction product from the phenylethynyl group is more thermo-oxidatively stable than that from a nadic endcapped material [24]. It was of interest to examine the isothermal aging properties of the PETI-298 and BMI-5270/AS-4 laminates. The laminates were cut into specimens and aged in a forced air oven. The effect of aging at 288°C in air on the OHC and SBS properties measured at room temperature are presented in Figures 4, 5 and 6.

As expected, the PETI-298 laminates exhibited dramatically higher retention of OHC strength after aging (Figure 4). The BMI-5270/AS-4 laminates exhibited nearly 50% reduction in strength after 500 hrs and had essentially no strength after 1000 hrs of aging. The PETI-298/AS-4 laminates exhibited 78% retention of unaged room temperature OHC strength after 1000 hrs of aging. The effect of aging on modulus (Figure 5) showed that the PETI-298/AS-4 laminates exhibited essentially no reduction in modulus whereas the BMI-5270/AS-4 laminates exhibited a 32% reduction after 1000 hrs. This is a direct reflection of the thermooxidative stability of these two different chemistries. The BMI-5270/AS-4 laminates exhibited nearly 50% reduction in strength after 500 hrs and had essentially no strength after 1000 hrs of aging. The PETI-298/AS-4 laminates exhibited 78% retention of unaged room temperature OHC strength after 1000 hrs of aging. The effect of aging on modulus (Figure 5) showed that the PETI-298/AS-4 laminates exhibited essentially no reduction in modulus whereas the BMI-5270/AS-4 laminates exhibited 32% reduction after 1000 hrs. The SBS strengths as a function of aging are presented in Figure 6. A similar trend was seen for this property, as that with the OHC strength, with the PETI-298/AS-4 laminates exhibiting ~63% retention of unaged room temperature SBS

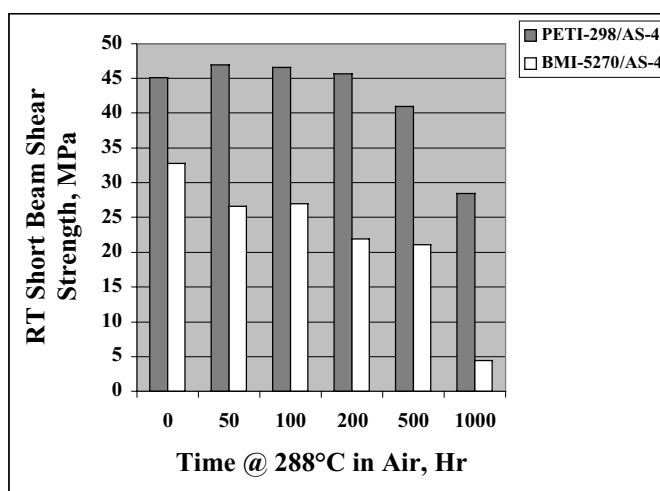
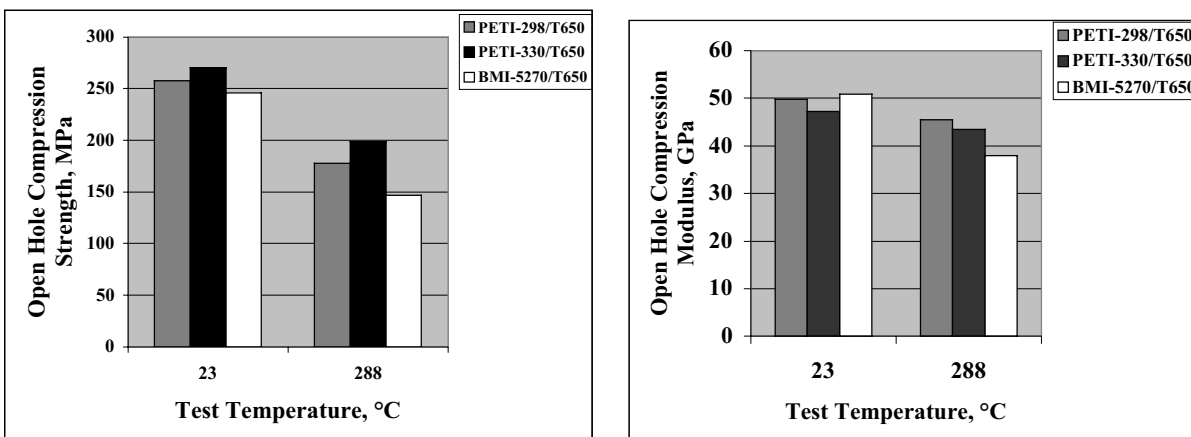


Figure 6. Effect of isothermal aging at 288°C in air on SBS strength measured at RT.

strength versus the BMI-5270/AS-4 laminates retaining only ~13% of their unaged room temperature SBS strength after 1000 hrs at 288°C in air. Since it is known that the thermooxidative stability of AS-4 carbon fibers is poor [25], T650-35, a carbon fabric often used for high temperature applications, was selected for use in subsequent laminate evaluation. Thus, PETI-298, PETI-330 and BMI-5270/T650-35 laminates were fabricated by RTM under the same conditions as those used to fabricate the AS-4 laminates. OHC properties determined at room



Figures 7 and 8. OHC strength and modulus of T650-35 laminates at 23 and 288°C.

temperature and 288°C are presented in Figures 7 and 8. SBS strengths as a function of temperature are shown in Figure 9.

As with the AS-4 laminates, the OHC strengths of all three resins on T650-35 fabric were comparable at room temperature. When tested at 288°C, the PETI-330/T650 laminates exhibited the highest OHC strength, followed by PETI-298 and the BMI-5270. When tested at 288°C, the PETI-330 exhibited retention of room temperature OHC strength of ~74%, followed by PETI-298 (~69%) and then BMI-5270 (~60%). The retention of OHC modulus at 288°C was higher for PETI-298 (91% of RT modulus) and PETI-330/T650 (92% of RT modulus) laminates as compared to the BMI-5270/T650 (75% of RT modulus) laminates. The SBS strengths as a function of temperature are presented in Figure 9. At the time of this work, PETI-298/T650 SBS samples were not available, thus the SBS strengths of PETI-330/T650 and the BMI-5270/T650 are compared. As expected, the PETI-330/T650 exhibited significantly higher SBS strengths at RT and elevated temperature. These specimens retained 62% of their RT SBS strength at 288°C. This is significantly less than that for the PETI-330/AS-4 SBS specimens which retained 88 %of the RT SBS strength at 288°C, although the absolute strength values were lower. The RT UNC strengths for PETI-298, PETI-330 and BMI-5270 T650 laminates were 457, 520 and 356 MPa, respectively.

The effect of isothermal aging at 288°C in air on OHC properties and SBS strengths were investigated. The effect on RT OHC strength and modulus of PETI-298/T650 and PETI-330/T650 are presented in Figures 10 and 11, respectively. For comparison purposes, BMI-

5270/AS-4 laminate properties are also included in the graphs. The effect of aging on OHC strength is comparable for both PETI-298 and PETI-330 T650 laminates with both retaining about ~78 % of their unaged OHC strength after 1000 hrs. The effect of isothermal aging on the

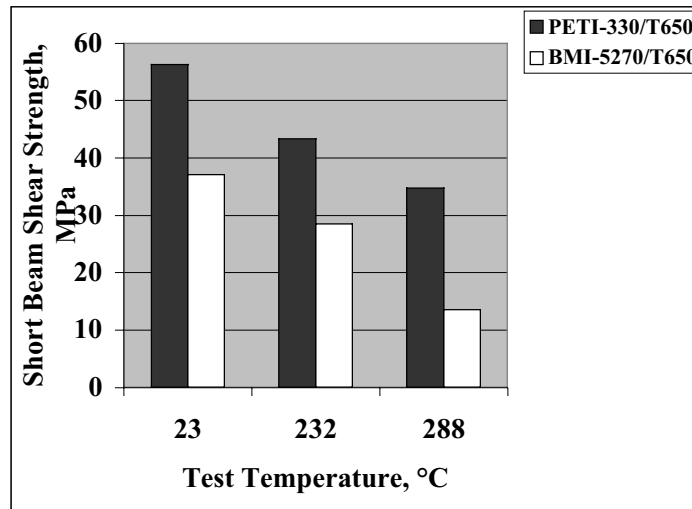
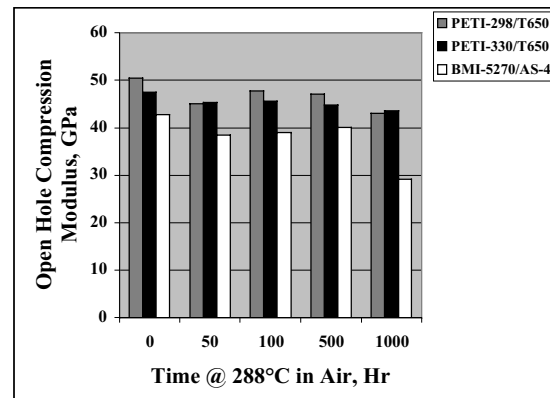
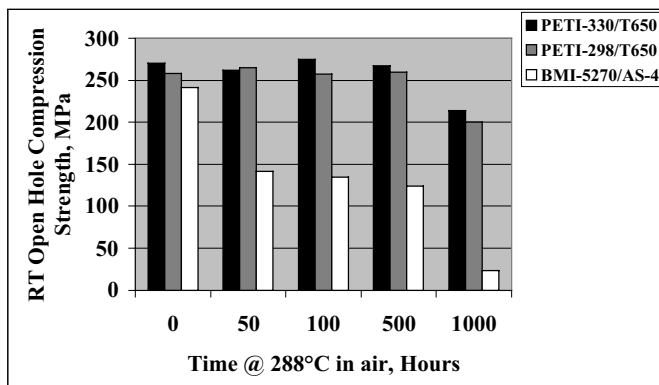


Figure 9. SBS strength of T650-35 laminates measured at 23, 232 and 288°C.

OHC modulus (Figure 11) was minimal with PETI-298 and PETI-330 T650 laminates retaining ~85% and ~92%, respectively of their unaged moduli after 1000 hours at 288°C in air. The effect of isothermal aging on the SBS strength is presented in Figure 12. In this case, PETI-298/T650 specimens were not available for aging, thus the data for PETI-298/AS-4 SBS specimens are included for comparison. The PETI-330/T650 specimens exhibited retention of



Figures 10 and 11. Effect of isothermal aging at 288°C in air on OHC strength and modulus.

~93% and ~75% of unaged RT SBS strength after 500 and 1000 hrs aging at 288°C in air, respectively. In contrast, the BMI-5270/T650 specimens retained ~73% and 40% of unaged RT SBS strength after 500 and 1000 hrs aging at 288°C in air, respectively.

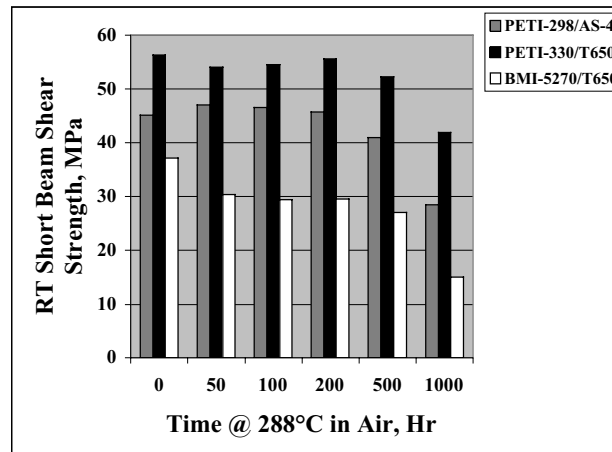


Figure 12. Effect of isothermal aging at 288°C in air on SBS strength measured at room temperature.

In comparing the properties of PETI-298 and PETI-330 on the two different fabrics (AS-4 and T650), the OHC strengths at RT and 288°C were comparable, however, the absolute values for the PETI-330 were higher, particularly at 288°C for the AS-4 laminates (87% retention on AS-4 versus 73% on T650). In comparing the OHC moduli, the absolute values were higher on T650 at RT, but when tested at 288°C, the absolute values were comparable for both the AS-4 and T650 laminates. With regard to the SBS strengths as a function of temperature, only the PETI-330 and BMI-5270 laminates are discussed since no SBS strength data was available on the PETI-298/T650 laminates. The PETI-330/T650 specimens exhibited higher SBS strength at RT and 232°C, however when tested at 288°C, the strengths were comparable for both the AS-4 and T650 PETI-330 specimens (~34 MPa). The PETI-330/AS-4 and T650 laminates exhibited higher SBS strengths than the comparable BMI-5270 laminates at all of the temperatures tested. Based on this data, no conclusions can be drawn to determine which fabric offers better mechanical properties. It was anticipated that some differences would become apparent upon isothermal aging of the laminates.

The isothermal aging was conducted on unstressed, specimens at 288°C in a forced air oven. The specimens were removed at various time intervals and subsequently tested at RT for OHC strength and modulus, and SBS strength. In comparing the OHC properties of PETI-298/AS-4 and PETI-298/T650 after aging, no significant difference in the OHC strengths was observed. They were very close in absolute strengths and in the retention of strength at every exposure interval. The OHC moduli were comparable except that the moduli of the T650 laminates were slightly higher. However, the retention of unaged modulus after aging for 1000 hrs was better on the PETI-298/AS-4 laminates (98% versus 85%). No obvious difference was observed in the mechanical properties as a function of aging that was attributable to the type of carbon fabric.

#### 4. SUMMARY

PETI-298, PETI-330 and BMI-5270 laminates were fabricated by high temperature RTM using unsized AS-4 and T650 carbon fabric. High quality laminates were prepared with void contents typically below 2%. Un-notched compression strength was determined at RT. Open hole compression properties and short beam shear strengths were determined at RT and elevated temperatures. Unstressed specimens were isothermally aged for 1000 hrs at 288°C in air and subsequently tested at RT. In general, the PETI-330 laminates exhibited higher mechanical properties than the PETI-298 laminates, most notably at elevated temperature. Both PETI-298 and PETI-330 laminates consistently exhibited higher mechanical properties than the BMI-5270 laminates at elevated temperatures. No significant difference in the retention of mechanical properties after aging was apparent for the PETI-298 and PETI-330 laminates, although the PETI-330 laminates typically had higher absolute values. The BMI-5270 laminates exhibited lower mechanical properties and significant reduction in properties after aging for 1000 hrs at 288°C in air. No obvious difference was observed in the mechanical properties of the composites upon isothermal aging that was attributable to the type of carbon fabric reinforcement. PETI-298 and PETI-330 transfer molding resins offer an unprecedented combination of processability, high temperature performance and toughness.

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